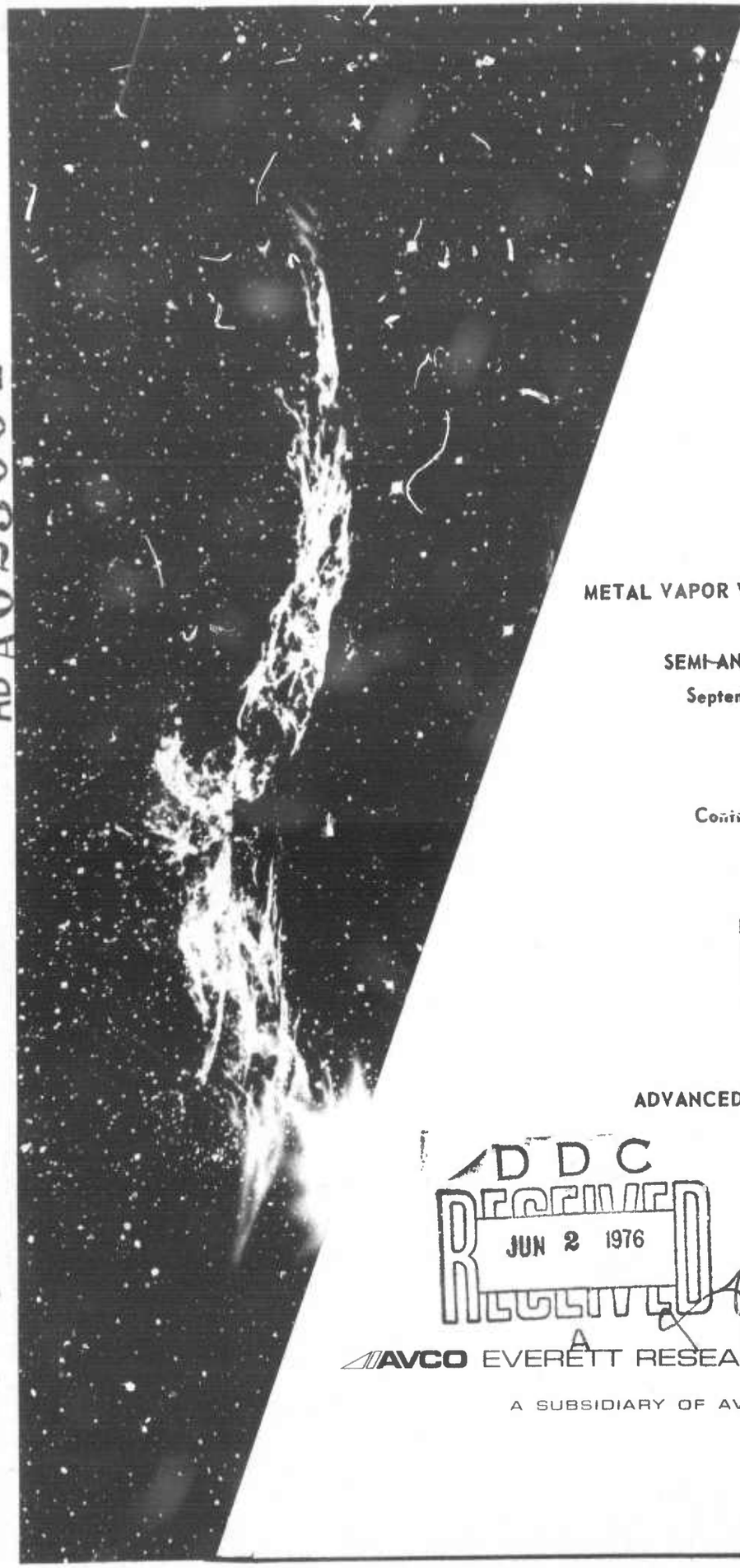

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METAL VAPOR VISIBLE LASER KINETICS PROGRAM

SEMI-ANNUAL TECHNICAL REPORT

September 1975 – February 1976

Contract No. N00014-75-C-0061

April 1976

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ARPA Order No. 1806

AVCO EVERETT RESEARCH LABORATORY, INC.

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2. Metastable Atom Quenching
3. Temperature Dependence of Metastable Atom Relaxation
4. Electronically Excited Bismuth Atoms
5. Resonance Absorption

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Objective: The objective of this program is to investigate experimentally and theoretically the important kinetic rate processes pertinent to the development of a high power visible laser. This research consists of three tasks. Each of the tasks are summarized below.

TASK I - LOWER LEVEL KINETICS (EXPERIMENTAL)

Objective: The purpose of this task is to identify metal atom systems that allow selective collisional relaxation processes to efficiency quench lower

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levels of potential or actual laser transitions. The present experimental study is directed to kinetic rate constant measurements for collisional relaxation of low-lying optically metastable states of lead, copper and bismuth.

Accomplishments: The flash photolysis apparatus developed under this contract was used to provide collisional quenching rate constants for deactivation of the $^2D^o_{5/2}$ and $^2D^o_{3/2}$ states of bismuth at room temperature. The high temperature experimental capability of the apparatus is currently being directed to provide temperature dependent rate constant data for collisional deactivation of these two low-lying optically metastable states.

TASK II - UPPER LEVEL KINETICS (EXPERIMENTAL)

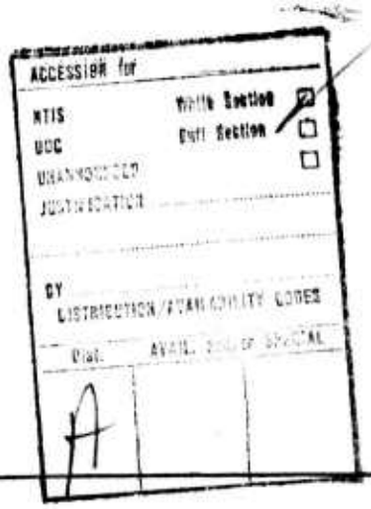
Objective: The purpose of this task is to determine the efficiency of various quenching gases in deactivating the upper laser level of lead. To be useful, a quenching gas must rapidly relax the lower laser level and slowly relax the upper laser level, i.e., be selective.

This task was completed and results reported in the Semi-Annual report covering the period March 1975 to August 1975.

TASK III - EXCITATION PROCESSES (THEORETICAL)

Objective: The objective of this effort is to calculate electron impact excitation and quenching cross section for the upper and lower laser levels of copper.

This task was completed and results reported in the Semi-Annual report covering the period March 1975 to August 1975.



FOREWORD

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Principal Investigator and Phone Number: Dr. D. Trainor
(617) 389-3000, Ext. 467

Scientific Officer: Director, Physics Program
Physical Sciences Division
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Arlington, Virginia 22217

Short Title of Work: Visible Metal Vapor Laser Kinetics

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

TASK I

LOWER LEVEL KINETICS

1. 1 INTRODUCTION

This task provides a kinetic data base to assess the likely suitability of various metal atoms as candidates for the construction of a high power, efficient visible laser. It consists of three subtasks, identified as to the particular metal atom under consideration, namely: (1) a measurement of the temperature dependence from 300 - 600°K of collisional relaxation rate constants for the $6p^2$ ($^3P_2$) and ($^3P_1$) states of atomic lead; (2) similar measurements for the $3d^9\ 4s^2$ ($^2D_{5/2}$) state of atomic copper at temperatures near 600°K; and (3) temperature dependent information on the $6p^3$ ($^2D^o_{3/2}$) and ($^2D^o_{5/2}$) states of bismuth.

1. 2 TEMPERATURE DEPENDENT LEAD RELAXATION EXPERIMENTS

This subtask has been completed and the results reported in the March 1975 Semi-Annual Technical Report. Additional information and a summary of results was included in the Semi-Annual Report covering the period March 1975 to August 1975.

1. 3 COLLISIONAL RELAXATION OF ELECTRONICALLY EXCITED COPPER

This subtask has been completed and the results reported in the Semi-Annual Report covering the period March 1975 to August 1975.

1. 4 TEMPERATURE DEPENDENT BISMUTH RELAXATION EXPERIMENTS

1. 4. 1 Introduction

Bismuth is a representative member of the group VA atoms, all of whose low lying electronic states are characterized by the np^3 electronic

configuration which gives rise to ^4S, ^2D, and ^2P states. Since these states all arise from the same electron configuration, they are optically metastable due to parity selection rules and, therefore, transitions between these states are optically forbidden. A partial energy level diagram showing the low-lying electronic states of atomic bismuth is shown in Fig. 1. Included in this figure are possible lasing transitions (allowed and forbidden) which have the common feature of terminating on the ^2D_J states. It may be appreciated from the information depicted in Fig. 1 that kinetic information describing collisional deactivation of these metastable ^2D_J states would be valuable in assessing the viability of building any successful, volumetrically scalable, bismuth metal vapor laser. In addition, information on techniques to rapidly and selectively pump the $^4P_{1/2}$ upper state is also needed.

It should be noted, however, that the allowed 4722 Å bismuth transition has not been made to lase by direct electron excitation. Various possible explanations have been offered, such as unfavorable electron excitation cross sections, possible $(Bi)_2$ dimer formation, etc.[1] It remains possible, however, to avoid these problems and produce laser action on this atom by utilizing near resonant electronic energy transfer pumping to populate the upper laser level. This might be done with a variety of excited species known to be readily produced in discharges, e.g., Hg $(^3P^o_{0,1})$, $N_2(A)$ state, etc. (see Fig. 2). These efficiently produced, high lying excited states have been experimentally observed to collisionally transfer some fraction of their available electronic energy into various metal atoms with large collision probabilities for transfer. For example, mercury $(^3P^o_1)$ being relaxed in collisions with sodium exhibits cross sections whose magnitudes range from 0.02 to 38.5 $Å^2$ depending on the

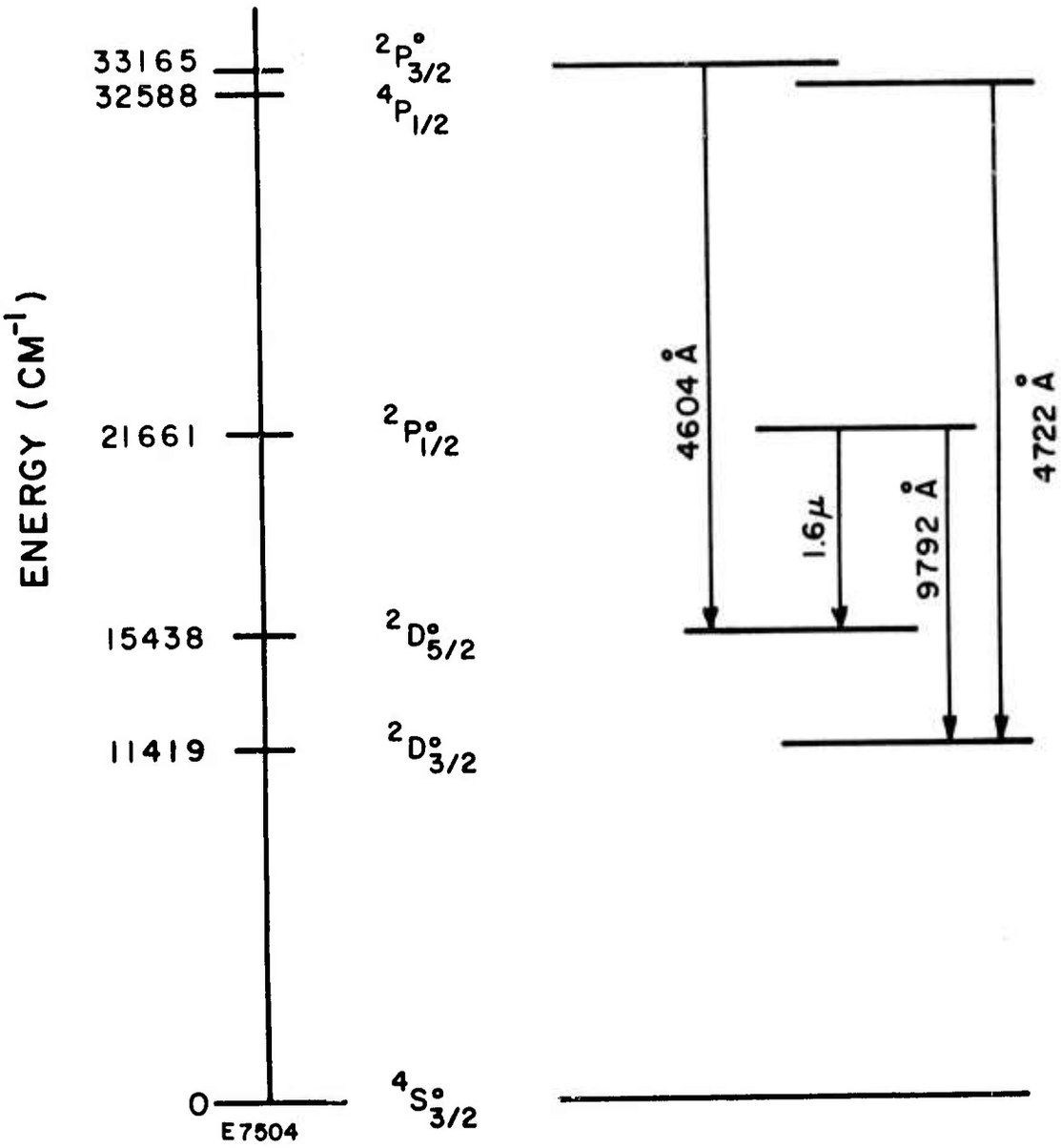

Fig. 1 Potential Bismuth Laser Transitions

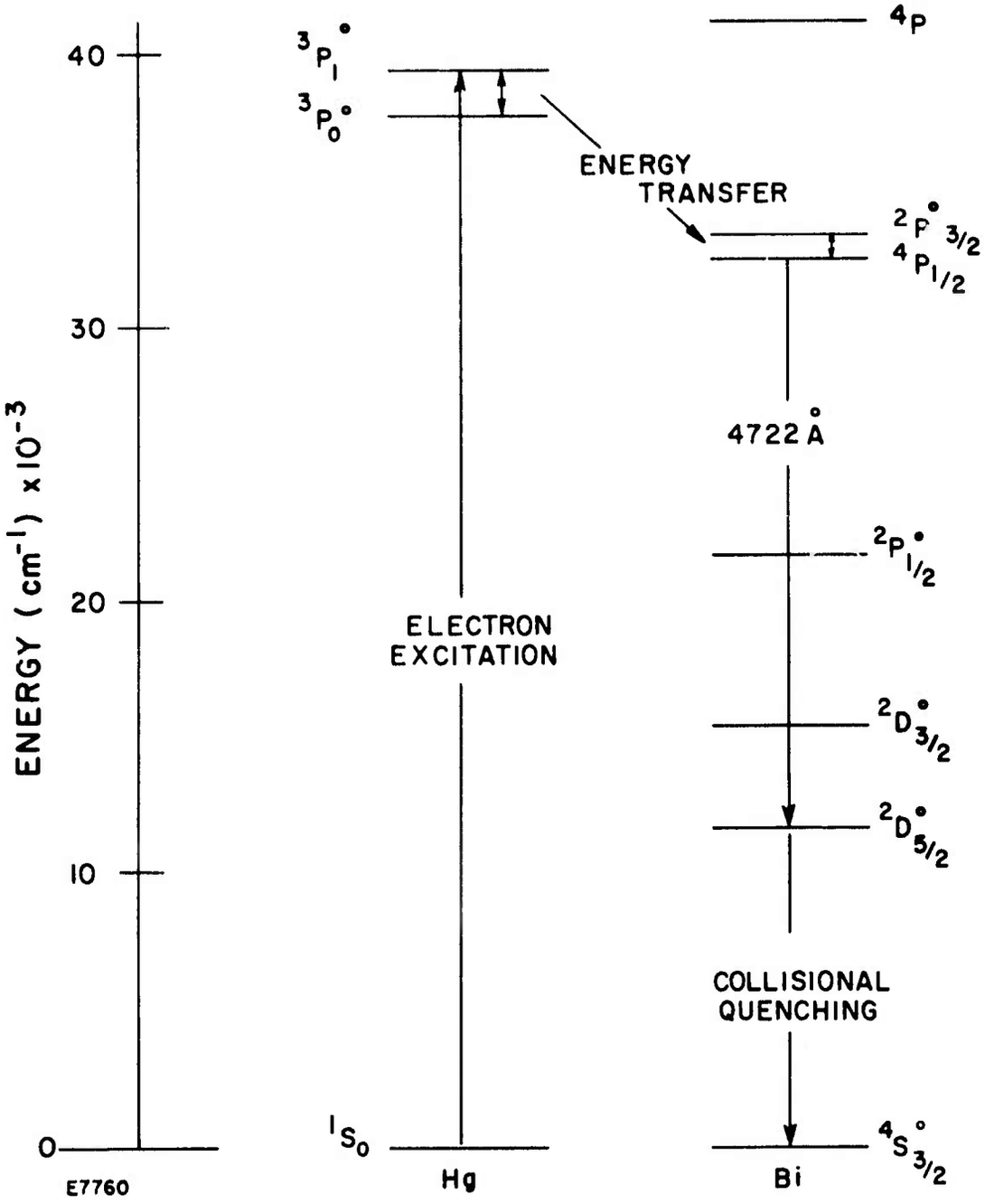

Fig. 2 Hg/Bi Energy Transfer Laser Concept

final state of the sodium.[2] Similarly, $N_2(A)$ state being relaxed in collisions with Hg atoms[3] proceeds with an overall cross section of about 60 $\AA^2$. Information on collisional transfer of energy from these species to bismuth is not available. Regardless of the upper level pumping scheme, quantitative measurements of lower level collisional quenching rates are important for scalable laser design. This subtask addresses this problem by providing temperature dependent kinetic rate constant information for collisional deactivation of the $^2D^o_{3/2}$ and $^2D^o_{5/2}$ metastable states of bismuth in collisions with atoms and simple molecules. In this report, rate constant measurements for the relaxation of these metastable states at room temperature in collisions with Ar, Xe, N_2, O_2, H_2, D_2, CO, CO_2, and SF_6 are reported. Information on the temperature variation of these rate constants over the range 300 - 600° will be included in the final report as these measurements are currently in progress.

In our experiment, these metastable states are produced by the multiphoton flash photolysis of trimethyl bismuth in an argon buffer gas which is used to maintain isothermal conditions. The production and subsequent time rate of decay of these excited state populations is monitored by time resolved resonance absorption spectroscopy at 2898 Å and 2938 Å for the $^2D^o_{3/2}$ and $^2D^o_{5/2}$ states respectively.

1.4.2 Experimental

The experimental approach is similar to our earlier studies on the lead system[4,5] and, therefore, will only be briefly described here. A schematic diagram of the apparatus is shown in Fig. 3. It consists of a Glomax hollow cathode light source, a 45 cm long reaction cell (1.8 cm i.d.) constructed of suprasil quartz with quartz windows fused to the cell itself,

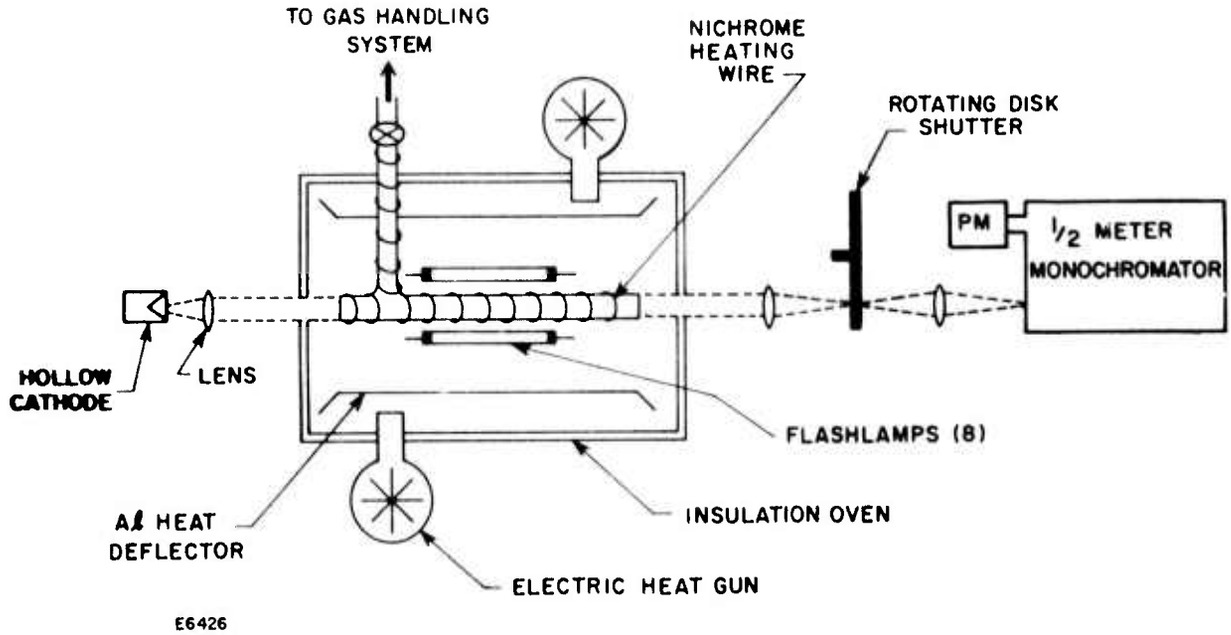

Fig. 3 Diagram of Apparatus

and a mechanical shutter/monochromator/photomultiplier detection system[6] for monitoring the resonance line selected for the time resolved absorption measurements.

In order to produce a nonequilibrium population of Bi ($^2D^o_{3/2}$) and ($^2D^o_{5/2}$) states, we flash photolyzed trimethyl bismuth (TMB). This organo-metallic compound exhibits a broad absorption band in the far-UV with a maximum near 2100 Å ($\epsilon = 1.65 \times 10^4$ ℓ mol^{-1} cm^{-1}).[7] The Bi (^2D_J) states are likely produced by sequential photo-dissociation of this volatile organo-metallic compound. The flashlamps consist of an array of eight linear suprasil quartz flashlamps (Xenon Corp and ILC Corp.) surrounding and parallel to the reaction cell. Each flashlamp typically dissipates 50 J/pulse. By choosing the concentration of trimethyl bismuth added to the reaction cell, we can control the quantity of excited ^2D_J states we produce in our flash apparatus. Reaction cell test gas mixtures at total pressures of 30 - 100 torr were made in large (3 and 12 liter) glass mixing flasks. These gas mixtures were mechanically stirred in the mixing bulbs long enough to produce homogeneous mixtures. The test cell, mixing manifold, and pressure gauges were pumped until the residual pressure was 10^{-5} torr and the leak plus outgassing rate was less than 10^{-4} torr/minute. For all cases, the primary impurities were those present in the gases themself.

The light source was a water cooled hollow cathode lamp (Barnes Engineering). The lamp intensity was monitored by a photomultiplier (1P28) mounted on a 1/2 meter monochromator whose output voltage was displayed on an oscilloscope for photographic recording. The $^2D^o_{3/2}$ state was monitored by absorption of radiation for transition to the $6p^2 7s\ ^2P_{1/2}$

state at 2897.98 Å. The $^2D^o_{5/2}$ state was monitored by absorption of radiation for transition to the $6p^2 7s\ ^2P_{3/2}$ state at 2938.30 Å. Under these experimental conditions, no evidence of any production of the $6p^3\ ^2P^o_{1/2}$ metastable state was observed. (See Fig. 4.)

Cylinder grade gases were used directly and were of the following purity based on the manufacturer's quoted values: Argon (Liquid Carbonic, 99.998%), Xenon (Research Grade, Matheson. 99.9999%), Nitrogen (Liquid Carbonic, 99.996%), Oxygen (Liquid Carbonic, 99.7%), Hydrogen (Matheson, 99.95%), Deuterium (Matheson, 99.5%), Carbon Monoxide (Research grade, Matheson, 99.99%), Carbon Dioxide (Research Grade, Matheson 99.995%), and Sulfur Hexafluoride (Mass Oxygen Equipment Co., 99.8%). The trimethyl bismuth (ALFA Products, 99.99%) was outgassed by several freeze, pump, thaw cycles before being mixed by successive dilutions with the argon buffer gas. For quenching rate measurements the TMB was present at concentrations less than 3 ppm. Quenching rates of bismuth by TMB quoted below are, of course, weighted averages for Bi, unphotolyzed TMB, methyl groups, fragments, etc.

1.4.3 Calibrations and Procedures

In order to relate the observed transmitted light intensity to the relative concentration of the particular metastable state under observation, we utilized the standard,[8] albeit controversial,[9] modified Beer-Lambert law, i.e.

$$I_{TR} = I_o \exp\left(-\epsilon[Bi^*]\ell\right)^{\gamma}$$

where ϵ is a constant, $[Bi^*]$ is the concentration of absorbing species, ℓ is the path length over which absorption occurs, I_{TR} the transmitted intensity of the bismuth line (which has an intensity I_o in the absence of absorption)

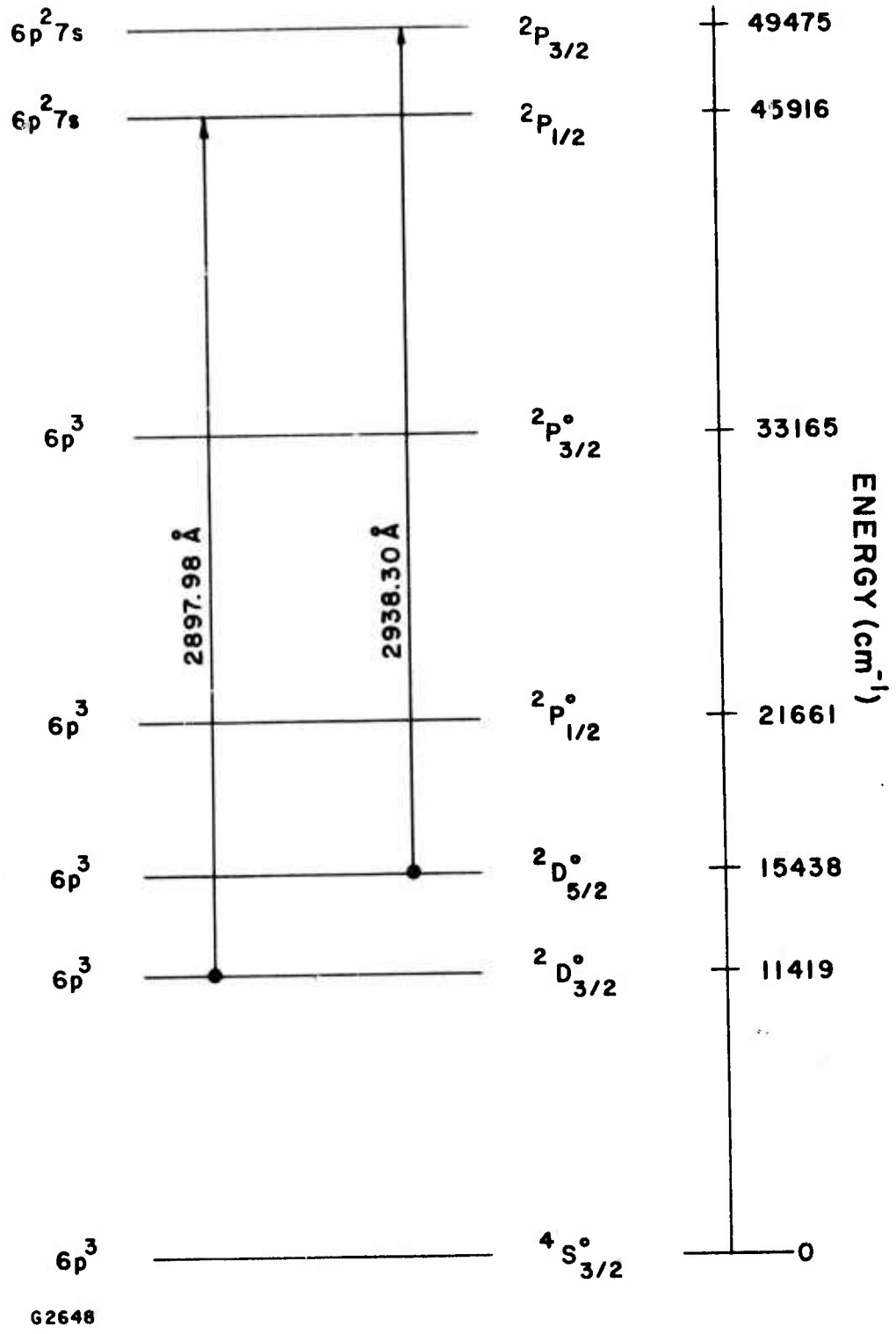

Fig. 4 Bismuth Partial Energy Level Diagram

chosen to monitor a particular Bi excited state, and γ is an experimentally determined constant. This reduces to the standard Beer-Lambert law for $\gamma = 1$. To obtain kinetic rate information on the pseudo first order decay of the excited states, we combine the solution for the first order kinetic rate equation

$$\ell n\,[Bi^*] - \ell n\,[Bi^*]_o = -k't$$

with the modofied Beer Lambert Law to obtain

$$\ell n\,\ell n\,(I_o/I) = \gamma\,\ell n\,[Bi^*]_{t=o} - \gamma k't + \text{const.}$$

From the intercepts of plots of $\ell n \ell n\,(I_o/I)$ vs time, we can generate a plot of $\ell n \ell n\,(I_o/I)_{t=o}$ vs $\ell n\,[Bi^*]_{t=o}$ by assuming that the quantity of Bi^* produced is proportional to the trimethyl bismuth present. Figure 5 gives such a plot for the Bi ($^2D^o_{3/2}$) state monitored at 2848 Å (see Fig. 4) in 50 and 100 torr of Argon buffer. These data are well fit by a value for γ near 0.8. Similarly, Fig. 6 gives a plot for the Bi ($^2D^o_{5/2}$) state monitored at 2938 Å in 25 and 75 torr of Argon. These data are well fit by a value for γ near 0.9. These results are summarized in Table I with the uncertainties in the value for γ determined by a least-square computer fit to these data.

A typical experimental sequence utilizes a baseline experiment with 0.09 μ or 0.18 μ trimethyl bismuth and 30 or 60 torr of argon for the $^2D^o_{3/2}$ and $^2D^o_{5/2}$ states respectively. Quenching in the baseline experiments is due to argon (or its impurities), the TMB, photofragments, and impurities in the organo-metallic. Subsequent experiments are then performed with new mixtures containing all the ingredients of the baseline experiment and an additional measured amount of the quenching gas under consideration.

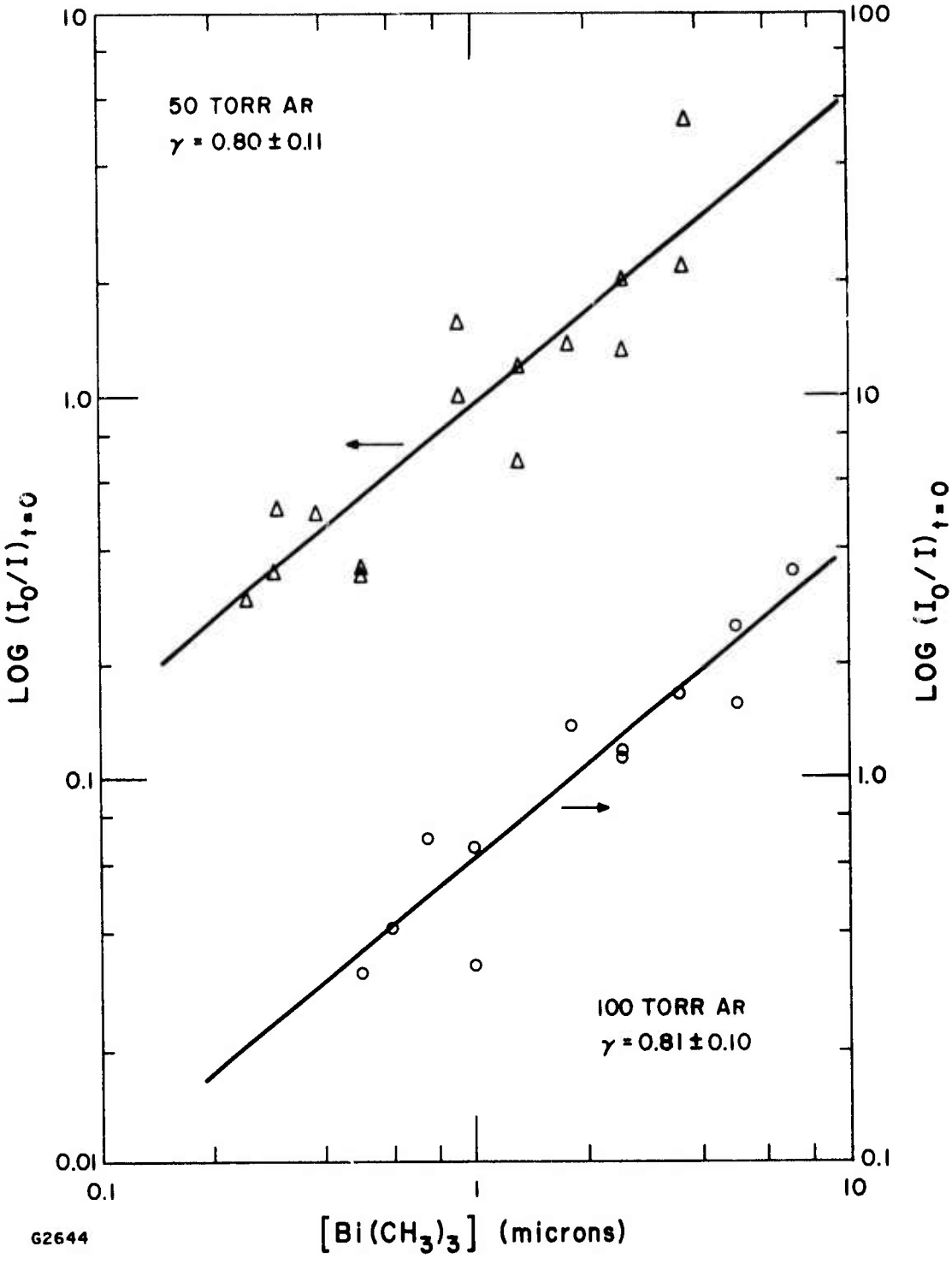

Fig. 5 γ - Plot for Bi $^2D^o_{3/2}$ State Monitored at 2848 Å

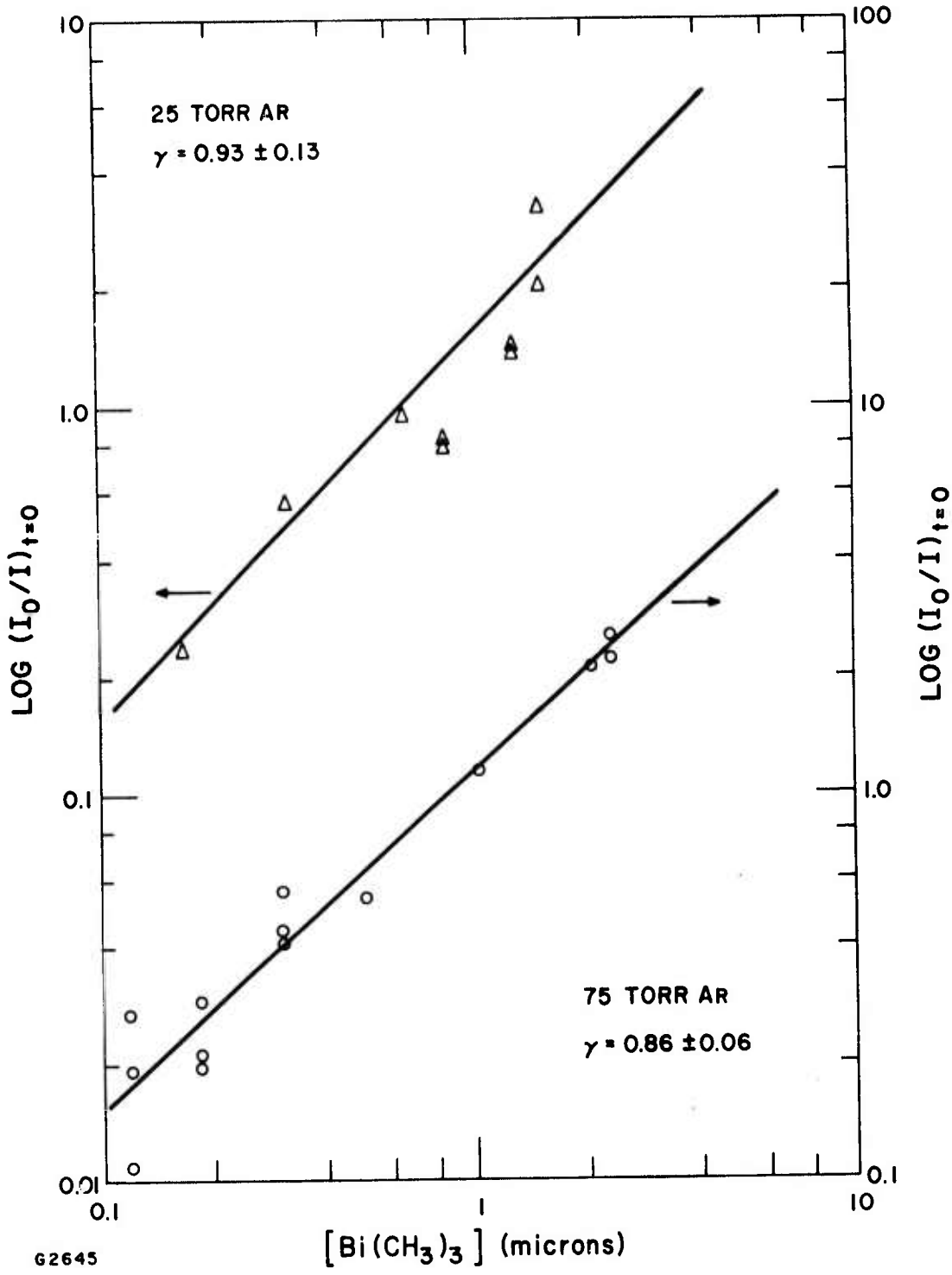

Fig. 6 γ - Plot for Bi $^2D^o_{5/2}$ State Monitored at 2938 Å

TABLE I

SUMMARY OF γ-VALUES FOR Bi $^2D^o_{3/2}$ and $^2D^o_{5/2}$ STATES

Transition[10]	λ, Å	gA x 10^{-8}, sec^{-1}[11]	[Ar], torr	γ
$6p^2 7s\ ^2P_{1/2} \rightarrow 6p^3\ ^2D^o_{3/2}$	2897.90	32	50	0.80±0.11
			100	0.81±0.10
$6p^2 7s\ ^2P_{3/2} \rightarrow 6p^3\ ^2D^o_{5/2}$	2938.30	61	25	0.93±0.13
			75	0.86±0.06

1. 4. 4 Results and Discussion

Figure 7 shows some typical data for the collisional deactivation of the Bi ($^2D^o_{3/2}$) state in mixes with and without added oxygen. Similarly, Fig. 8 shows data for the collisional relaxation of the Bi ($^2D^o_{5/2}$) state in mixes with and without added carbon dioxide. The slopes of these first order decay plots provide values for $-\gamma k'$, where k' is the pseudo first order rate constant describing all occurring relaxation processes, i. e.

$$\gamma k' = k_{Ar}[Ar] + \sum_i k_i [N_i] + k_q [Q],$$

where $k_{Ar}[Ar] + \sum_i k_i[N_i]$ represents the decay of Bi^* due to collisions with the species present in the baseline mix and is taken to be a constant. Therefore, a plot of k' vs $[Q]$, the quenching gas density, provides a relationship for determining the absolute second order quenching rate constant, k_q, for a number of quenchers. A typical plot is shown in Fig. 9 for the relaxation of the Bi ($^2D^o_{3/2}$) in collisions with molecular oxygen. Similar data were collected for the relaxation of these metastable states in collisions with Ar, Xe, N_2, H_2, D_2, CO, CO_2, O_2 and SF_6. These data are summarized in Table II. Where uncertainties are indicated, they represent one standard deviation of a least-square computer fit to the data.

Rate constants are reported as upper bounds when the ratio of the derived rate constant to the gas kinetic rate constant ($k_{GK} = 2 \times 10^{-10}$ cm^3/sec) is less than the mole fraction of manufacturer's stated level of impurities in the quenching gas. This is necessary because of our uncertainty in assigning the observed increase in $\gamma k'$ to the quencher under investigation or to the impurities which come with the quencher.

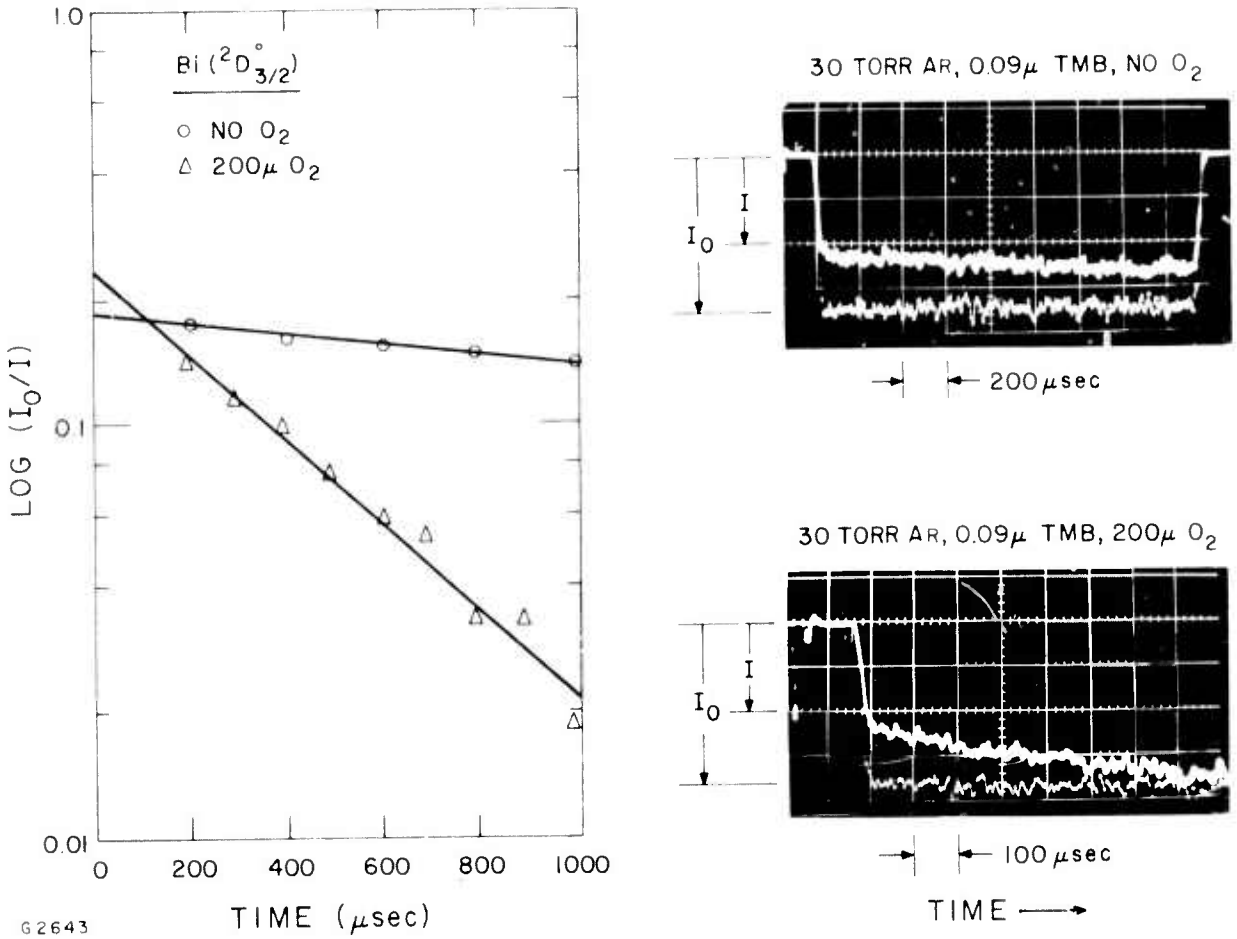

Fig. 7 Typical Data for the Relaxation of Bi $^2D^o_{3/2}$ State in Collisions with O_2

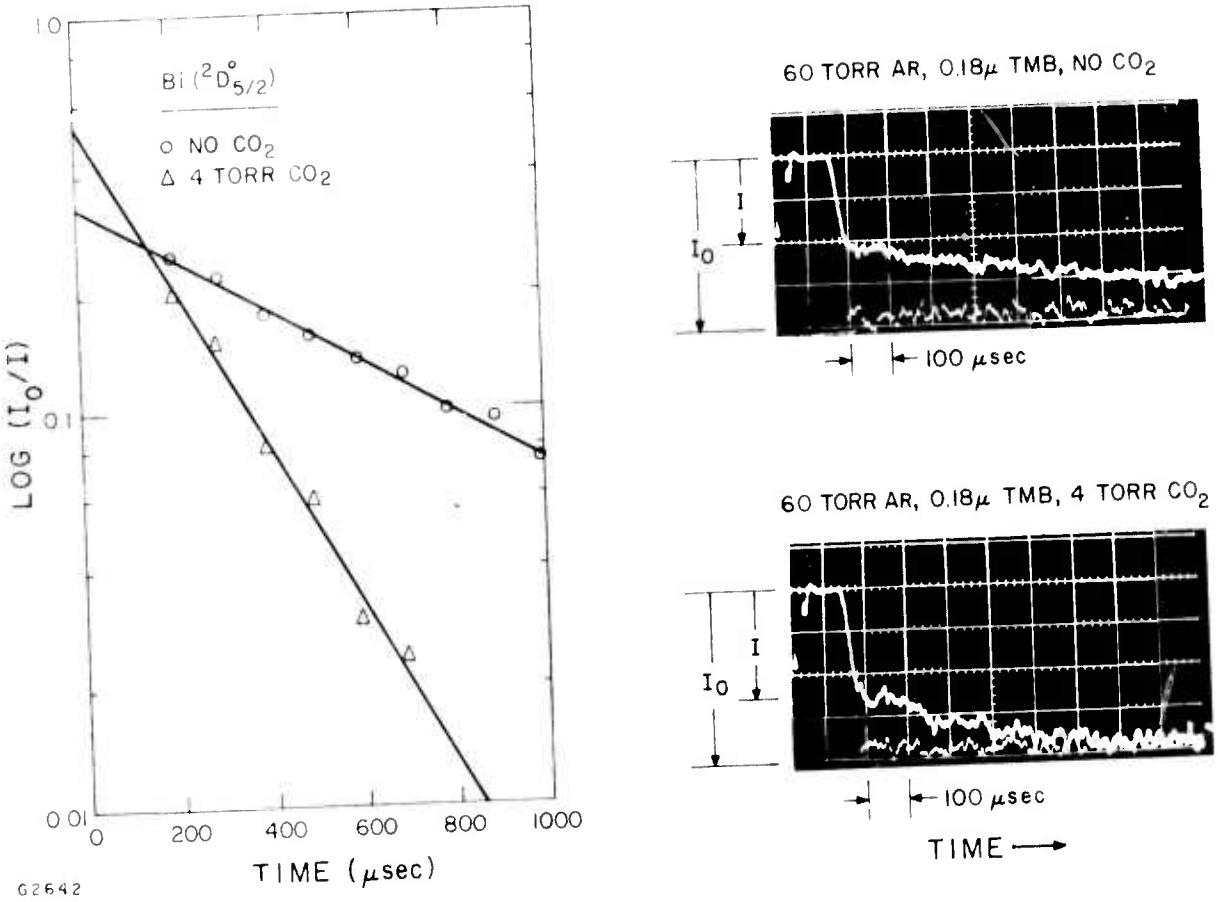

Fig. 8 Typical Data for the Relaxation of Bi $^2D^o_{5/2}$ State in Collisions with CO_2

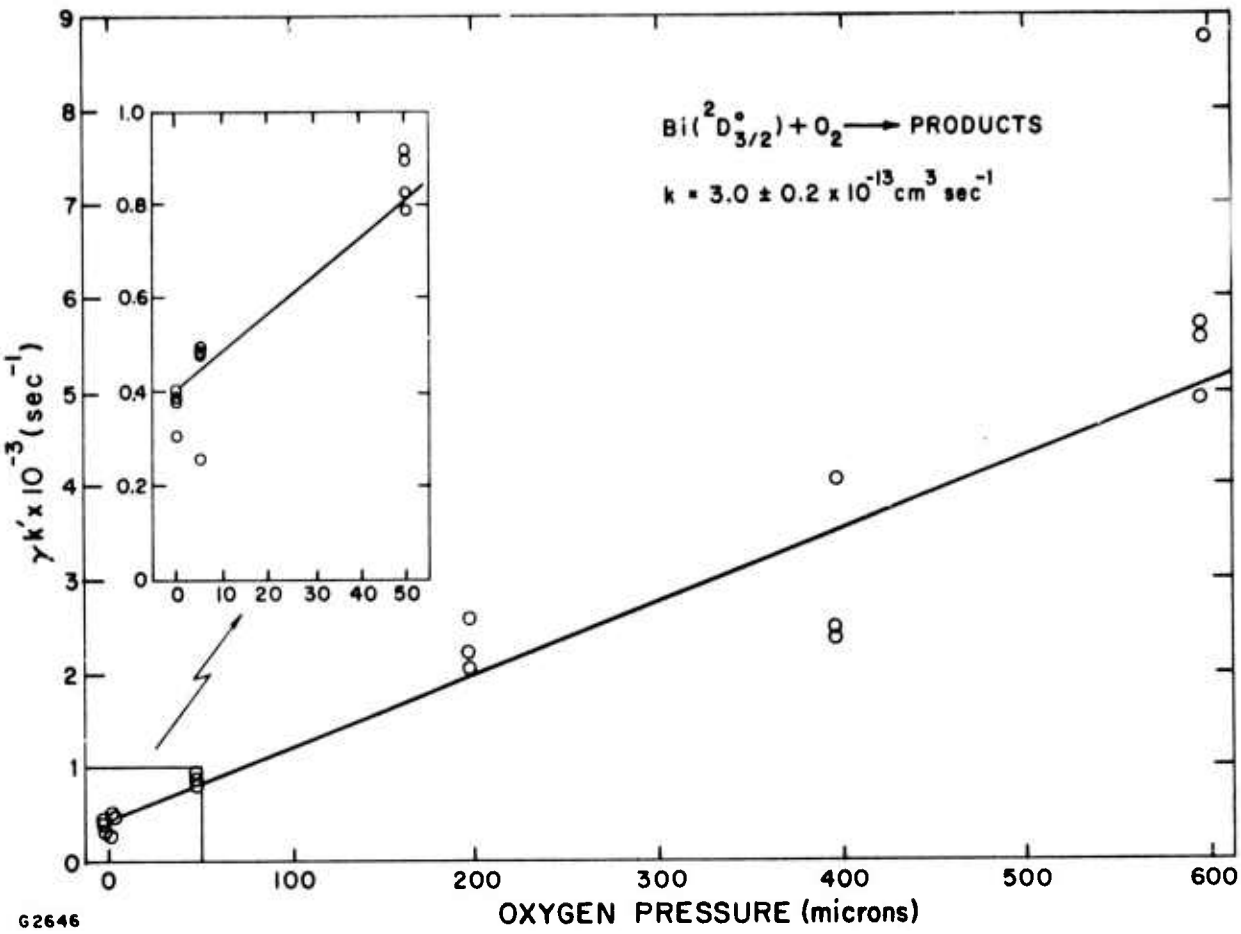

Fig. 9 Plot of Pseudo First Order Rate Constant, γk, vs O_2 Pressure

TABLE II

SUMMARY OF KINETIC RATE CONSTANTS AT 298°K

$k\ (cm^3/sec)$

	$Bi\ ^2D^o_{3/2}$	$Bi\ ^2D^o_{5/2}$
TMB	$1.2\pm0.1 \times 10^{-10}$	$6.9\pm0.5 \times 10^{-11}$
Ar	$< 1 \times 10^{-16}$	$< 4 \times 10^{-16}$
Xe	$< 1.2^{+1.7}_{-1.2} \times 10^{-16}$	$1.9\pm0.3 \times 10^{-15}$
N_2	$< 0 \pm^{1.9}_{0} \times 10^{-16}$	$< 6.3\pm2.9 \times 10^{-16}$
H_2	$7.2\pm0.3 \times 10^{-15}$	$1.0\pm0.7 \times 10^{-11}$
D_2	$< 2.5\pm1.6 \times 10^{-16}$	$1.1\pm0.6 \times 10^{-13}$
CO	$1.4\pm0.6 \times 10^{-15}$	$4.7\pm0.2 \times 10^{-13}$
O_2	$3.0\pm0.2 \times 10^{-13}$	$1.7\pm0.1 \times 10^{-11}$
CO_2	$\sim 1 \times 10^{-15}$	$\sim 3 \times 10^{-14}$
SF_6	$\sim 6 \times 10^{-16}$	$\sim 2 \times 10^{-15}$

The usual approach in discussing these types of quenching results is to consider the specific energetics and symmetry correlations among each combination of reactants and possible likely product channels.[12] Such detailed interpretation will be more easily formulated when the temperature variation of these rate constants has been measured. This additional information will provide added insight into likely deactivation mechanisms. Since it is anticipated this measurements will be completed in the remaining contract performance period, we will delay detailed interpretation until all the experimental information is available.

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